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(21) International Application Number: PCT/US91/00015 (22) International Filing Date: 8 January 1991 (08.01.91) (30) Priority data: 464,434 12 January 1990 (12.01.90) US (60) Parent Application or Grant (63) Related by Continuation US 464,434 (CON) Filed on 12 January 1990 (12.01.90) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		(72) Inventor; and (75) Inventor/Applicant (for US only) : TOCKER, Stanley [US/ US]; 4656 Norwood Drive, Wilmington, DE 19803 (US). (74) Agents: KATZ, Elliott, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Mar- ket Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CA, CH (European patent), DE (Euro- pean patent), DK (European patent), ES (European pa- tent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (Euro- pean patent), SU, US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: PROCESS FOR PREPARING CONTROLLED RELEASE GRANULES (57) Abstract Process for preparing controlled release granules of pesticides for direct application consisting essentially of overcoating a granular carrier containing a pesticide and a di- or polyhydroxylated compound or water with a liquid polyisocyanate and a polymerization catalyst optionally at elevated temperatures, resulting in interfacial polymerization to a solid cross-linked polyurethane or polyurea barrier.		

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TITLE

PROCESS FOR PREPARING CONTROLLED RELEASE GRANULES

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BACKGROUND OF THE INVENTION

This invention relates to a simplified process for preparing controlled release granules of pesticides.

Controlled release pesticides in granular formulations have been well known in the art for quite some time.

U.K. Patent Application No. 2,007,095-A discloses a process for making slow release biologically active granules by mixing an active with a polyisocyanate and one or more compounds having an active hydrogen atom and then granulating. The granulation operation requires specialized equipment such as a fluidized bed or spray dryer.

U.S. 4,223,070 discloses a process for making slow release granules involving overcoating inert porous granules with a solution of active and an organic polyisocyanate followed by applying an aqueous solution of polymerization catalyst as an additional step.

Japanese Patent Application No. 58-82303 (Kokai No. 59-206302) discloses a process involving coating an active component on a granular carrier with a hydroxyl-containing organic compound or water, a "non-ionic surfactant" of the formula $RO(CH_2CH_2O)_nCONHX$ where R is C_1-C_4 alkyl, n is 1-120, and X is a di- or polyisocyanate residue, and a polyisocyanate.

A need still exists, however, for improved controlled release granules prepared by a simple process in conventional mixing equipment.

4772 490

According to the instant invention, an improved process for preparing controlled release granules has been found which is much more versatile and convenient than the processes mentioned above. No adjuvants or solvents are required in the process of this invention. Treatment with aqueous catalyst solution as taught in U.S. 4,223,070 is not required, and such treatment could lead to non-uniform polymeric coatings because of non-uniform wetting. The process of the present invention can be applied to porous or nonporous granules whereas the process of U.S. 4,223,070 is applicable only to the former. Also, the process of U.S. 4,223,070 requires that the active component be dissolved in the polyisocyanate whereas the process of this invention does not have this requirement. Many pesticides do not dissolve in polyisocyanates and in some cases, the biologically active material can be destroyed by reaction with the polyisocyanate.

SUMMARY OF THE INVENTION

This invention relates to a process for preparing controlled release granules of pesticides for direct application consisting essentially of overcoating a granular carrier containing a pesticide and a polyhydroxylated compound or water with a liquid polyisocyanate and a polymerization catalyst, optionally at elevated temperatures, resulting in interfacial polymerization to a solid cross-linked polyurethane or polyurea barrier.

The term pesticide refers to water-soluble or water-insoluble chemicals commonly known as herbicides, fungicides, insecticides, nematocides, acaricides, miticides, virucides, algicides, bactericides, plant growth regulants, and their

agriculturally suitable salts. Preferred are those pesticides which lend themselves to direct soil application. More preferred are herbicides selected from the classes of herbicidal sulfonylureas, imidazolinones, uracils and dinitroanilines; and insecticides selected from the classes of insecticidal carbamates and phosphonates. Specifically preferred are the following:

methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]methylbenzoate (bensulfuron);

5-bromo-3-sec-butyl-6-methyluracil (bromacil);

α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine (trifluralin);

N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide (oxamyl);

S-tert-butylthiomethyl O,O-diethylphosphorodithioate (terbufos); and

O,O-diethyl O-(1,2,2,2-tetrachloroethyl)-phosphorothioate.

Granular carrier refers to any inert porous or nonporous solid material, examples of which include sand, aggregated clays such as kaolinite, bentonite and attapulgite, vermiculite and granular salts or organic compounds such as sugars, urea, potassium or calcium carbonate, ammonium nitrate, and other granular fertilizers. The term granular carrier also includes water-dispersible granules, examples of which are Glean® 75 DF, Pinnacle® DF and Londax® 60 DF, products of E. I. du Pont de Nemours and Company, Wilmington, DE. Preferred granule size is about 150 to 4000 microns with 250 to 2000 microns being more preferred.

The term polyhydroxylated compound refers to organic chemicals containing two or more free hydroxyl substituents, examples of which include glycols, glycerin or other polyhydric alcohols or mixtures thereof which are liquids or low-melting solids. Preferred are ethylene glycol or propylene glycol.

The term polyisocyanate refers to any aliphatic, alicyclic or aromatic organic compound with two or more isocyanato substituents (-NCO) present, which is either a low-melting solid or is a liquid at ambient temperature and pressure. Examples of suitable polyisocyanates include the following:

hexamethylene-1,6-diisocyanate;
m-phenylene diisocyanate;
p-phenylene diisocyanate;
2,4-toluene diisocyanate;
2,6-toluene diisocyanate;
1,5-naphthalene diisocyanate;
cyclohexane 2,4-diisocyanate;
1-methylcyclohexyl 2,6-diisocyanate; and
2,4,6-triisocyanato toluene;
or mixtures thereof that are liquids.

Preferred are methylene-linked polyphenylisocyanates, examples of which include those sold under the trade names "Mondur MRS®" (Mobay Chemical Co.) and "PAPI®" (Dow Chemical Co.); the latter is more preferred.

Suitable polymerization catalysts are organic tertiary amines and alkyltin carboxylic esters. Preferred catalysts are triethylamine, trimethylamine, triethylen diamine, tri-n-butylamine, N-methyl-morpholine, tri thanolamine, dibutyltin dilaurate, dibutyltin diacetate, tributyltin acetate,

dibutyltin laurate and dibutyltin maleate. More preferred is dibutyltin dilaurate.

5 The process is carried out by adding the polyisocyanate and polymerization catalyst to the granules containing the pesticide and water or polyhydroxylated compound at ambient temperature or above. The preferred temperature range is about 23°C
10 to 35°C. The amounts of polyisocyanate and polymerization catalyst employed in the reaction are about 1 to 20% and 0-5% by weight, respectively; a more preferred amount of catalyst is 0.05-1%. More
15 than 20% by weight of the polyisocyanate can be added to the granule if it is applied stepwise, e.g., in layers. The water or polyhydroxylated material must be present in an amount sufficient to ensure that all of the polyisocyanate has reacted. Although reaction time is not critical, it is preferred that the
20 granules can be easily handled (i.e., are nonaggregating) after about 20-30 minutes; a more preferred length of time is about 20 minutes.

DETAILED DESCRIPTION OF THE INVENTION

25 The granular bases used in the process of this invention can be aggregated minerals, clays and other inorganic substances or organic mixtures prepared by known methods such as granulating, prilling, tableting, extrusion or compacting. The granular bases can also be naturally occurring granules such
30 as sands. Examples of suitable inorganic granular bases include kaolinite, bentonite, attapulgite, vermiculite crushed brick and granular salts. Nonlimiting examples of suitable organic granular bases includ sugars, urea, potassium carbonate and
35 calcium carbonate. Other suitable materials include granulated corn cobs. The process of this invention

is also applicable to commercial water dispersible granules prepared by granulation of powdered premixes of biologically active materials and formulation adjuvants such as binders and dispersants. Preferred are inert aggregated mineral granules which are impregnated with active material. Preferred granule size is about 150 to 4000 microns with 250 to 2000 microns being more preferred.

The active material used in the process of this invention can be a mixture of compounds or a single compound, and can be in the form of a solid or liquid. The active material can be an integral part of the granule matrix or can be added at any time during the processing as will be apparent to one skilled in the art. It is preferred that the active material be a component of the granular material used or be mixed with or impregnated into the granular matrix prior to overcoating with polymer. One advantage of pre-incorporation is that there would be less opportunity for the active material to react with the polyisocyanate in cases where the active material is a compound containing hydroxyl, amino, carboxylic acid or other similarly reactive functional groups. Also, by integrating the active material present in or placing it on the granular base before the polymer barrier is formed, superior barrier characteristics are attainable with relatively small amounts of polymer. In this manner, the polymer barrier is not diluted or weakened by the presence of a non-polymeric material. However, when desired, non-volatile organic material or the active material can sometimes be advantageously added to the polyisocyanat for adjustment of release rate.

Suitable active materials are selected from the group consisting of herbicides, fungicides, insecticides, nematocides, acaricides, miticides, virucides, algicides, bactericides and plant growth regulants, and their agriculturally suitable salts. Preferred are those active materials which lend themselves to direct soil application. More preferred are herbicides selected from the classes of sulfonylureas, imidazolinones, uracils and dinitroanilines; and insecticides selected from the classes of carbamates and phosphonates. Specific examples of preferred active materials are the following:

methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]methylbenzoate;
5-bromo-3-sec-butyl-6-methyluracil;
 α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine;
N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide;
S-tert-butylthiomethyl O,O-diethylphosphorodithioate; and
O,O-diethyl O-(1,2,2,2-tetrachloroethyl)-phosphorothioate.

The term "polyhydroxyl compound" as used in the context of this invention is meant to include organic compounds containing at least two free hydroxyl (-OH) substituents. Examples of suitable polyhydroxyl compounds include glycols, glycerin and other polyhydroxylated alcohols or mixtures thereof, or mixtures thereof with water, which are either liquids or solids. Preferred polyhydroxyl compounds are ethylene glycol and propylene glycol. Water can be

used in place of some or all of the polyhydroxyl compound or mixture or polyhydroxyl compounds. While
5 solid polyhydroxyl compounds are operable in the process of this invention, it is preferred that they be used in liquid form by dissolution in a second, liquid polyhydroxyl compound.

The term "polyisocyanate" as used in the
10 context of this invention is meant to include any organic compound containing at least two isocyanato (-NCO) substituents. When solid polyisocyanates are employed in the process of this invention, it is preferred that they be pre-dissolved in a second,
15 liquid polyisocyanate.

Preferred polyisocyanates are methylene-linked polyphenylisocyanates, nonlimiting examples of which include those sold under the trade names "Mondur MRS®" (Mobay Chemical Co.) and "PAPI®" (Dow Chemical
20 Co.); the latter is more preferred.

While the polymerization reaction requires no catalyst and can be accelerated solely by heating, it is preferred that the process be completed in under 60 minutes, most preferred under 30 minutes at room
25 temperature. The polymerization reaction can be accelerated to provide this result by addition of known catalysts for preparing ureas and urethanes, such as organic tertiary amines or alkyltin carboxylic esters to the polyisocyanate before
30 application to the granular substrate. Preferred catalysts are triethylamine, trimethylamine, triethylenediamine, tri-n-butylamine, N-methylmorpholine, triethanolamine, dibutyltin dilaurate, dibutyltin diacetate, tributyltin acetate,
35 dibutyltin laurate and dibutyltin maleate. More preferred is dibutyltin dilaurate.

The process of this invention is carried out by adding the polyisocyanate and optional polymerization catalyst to the granules containing the active material and water or polyhydroxyl compound at ambient temperature or above. The preferred temperature range is about 23°C to 35°C. The amount of polyisocyanate employed in the process is about 1 to 20% by weight based on the amount of granular material. Greater than 20% by weight of polyisocyanate can be added to the granules if it is applied in sequential layers wherein sufficient time is allowed for each layer to polymerize before the next coating is applied. When a polymerization catalyst is used, the preferred amount is up to about 5% by weight relative to the amount of polyisocyanate; a more preferred amount of catalyst is 0.05 to 1%. The catalyst is most advantageously applied in solution with the polyisocyanate or polyhydroxyl material to achieve a uniform polymerization reaction. The water or polyhydroxyl compound must be present in an amount sufficient to insure that all of the polyisocyanate has reacted. The barrier-forming reaction occurs at the interface between the top layer of the isocyanate phase and the underlying water or hydroxyl material and generally continues until all the isocyanate functionality is consumed. The presence of excess water or hydroxyl functionality does not normally affect the barrier since such material can be entrapped under the barrier formed. Although reaction time is not critical, it is preferred that the granules can be easily handled (i.e., are nonaggregating) after about 20 to 30 minutes; a more preferred length of time is about 20 minutes.

Where water is the coreactant with the polyisocyanate, some of the isocyanate groups hydrolyze to form amino functionality, followed by self-polycondensation by reaction with the unaffected isocyanate groups. Under these conditions, a polyurea is formed. Where a polyhydroxyl compound is used, a polyurethane is produced as barrier. When the polyhydroxyl or polyisocyanate compounds have more than two hydroxyl or isocyanate groups, cross-linked polymeric barrier coatings are formed. If a mixture of water and at least one organic polyhydroxyl compound is used, the polymeric barrier produced is a polyurea-urethane.

Reduction of the release rate is generally achieved by use of aromatic polyisocyanates instead of aliphatic polyisocyanates or by increasing the amount of polymer forming ingredients (which governs the thickness of the shell). Reduction of release rate can also be achieved by increasing the degree of cross-linking by using reactants containing more than two hydroxyl or isocyanate groups to process cross-linking and using no diluents.

In the Examples below, which are further illustrative of the process of this invention, release rates were measured in pH 7 buffered water at room temperature under static conditions. In all cases, sufficient water was used to greatly exceed the quantity needed to dissolve all the active material. The water was agitated just prior to sampling to insure an even concentration of dissolved active. The concentration of active was measured by HPLC. Percentages are meant to be weight percentages unless otherwise indicated.

EXAMPLE 1

Granules of the insecticide O,O-diethyl
5 O-(1,2,2,2-tetrachloroethyl)phosphorothioate (4.08 g)
containing 4% propylene glycol and 10% of the active
ingredient were mixed with 1.0 g of a solution of
0.01 g dibutyltin dilaurate in PAPI® 901 (Dow
Chemical Co.). After 30 minutes, the granules were
10 free-flowing. The volatility of O,O-diethyl
O-(1,2,2,2-tetrachloroethyl)phosphorothioate in these
coated granules was compared with unmodified granules
at 45°C-60°C in an air oven. After 44 hours, the
overcoated granules lost 0.12 g active ingredient
15 while the uncoated sample lost 0.27 g thereby showing
that the polymeric coating retarded volatilization of
the active ingredient.

EXAMPLE 2

Water-dispersible granules containing 60% of
20 methyl 2-[[[4,6-dimethoxy-2-pyrimidinyl)amino]-
carbonyl]amino]sulfonyl]methylbenzoate (9.0 g;
Londax® 60 DF; E. I. du Pont de Nemours and Company)
were mixed with 0.3 g propylene glycol followed by a
solution of 1.0 g PAPI® 901 (Dow Chemical Co.) and
25 0.01 g dibutyltin dilaurate. After standing in an
open beaker for about 30 minutes, the somewhat sticky
mixture became free-flowing, indicating that
polymerization to polyurethane coating had occurred.
The granules were added to 500 mL water and were
30 allowed to stand 3 days. The granules maintained
their integrity while slowly releasing some of the
active ingredient: 12% in 21 hours, 31% in 46 hours,
and 100% in 300 hours. The uncoated granules
completely disintegrated in excess water in about 2
35 minutes and released 100% of the active in under 2
hours.

EXAMPLE 3

Florex® LVM 8-16 mesh attapulgite granules
5 (Florex LVM) (Floridin Co.) were preimpregnated with
polymer, to reduce porosity, by mixing 120 g of the
material with 5 g propylene glycol followed by 10 g
of PAPI® 901 containing 0.5% dibutyltin dilaurate.
After allowing 1 hour for curing to a crosslinked
10 polyurethane containing, 16.6 g of the precoated
granules were mixed with 0.627 g technical
2-[[[[4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-
amino]sulfonyl]methylbenzoate (95.7%), 0.39 g
propylene glycol followed by 0.8 g PAPI® 901
15 (Dow Chemical Co.) containing 0.02 g dibutyltin
dilaurate. The sample was allowed to cure in an open
vessel giving a product having 3% active ingredient
with crosslinked polyurethane urea overcoat. The
release rate in excess pH 7 buffered water was 15% in
20 162 hours and 24% in 451 hours.

EXAMPLE 4

Sand (76.4 g, diameter 250 to 840 microns) was
mixed with 0.2 g propylene glycol followed by 0.6 g
PAPI® 901 containing 0.063 g dibutyltin dilaurate.
25 Then 2.5 g of 2-[[[[4,6-dimethoxy-2-pyrimidinyl)-
amino]carbonyl]amino]sulfonyl]methylbenzoate powder
was added with stirring to give a mixture containing
3% active ingredient. After curing had occurred, the
release rate in excess pH 7 buffered water was found
30 to be 42% in 67 hours and 96% in 499 hours.

EXAMPLE 5

Example 4 was repeated, except that the PAPI®
901 solution was added last, giving granules that
r leased somewhat slower, 35% in 114 hours and 74% in
35 525 hours.

EXAMPLE 6

Example 4 was repeated except for the
5 substitution of propylene glycol by 0.16 g water.
Release rates for the polyurea coating were 63% in
305 hours and 100% in 665 hours.

EXAMPLE 7

Sand (17.3 g), 0.627 g 2-[[[4,6-dimethoxy-
10 2-pyrimidinyl)amino]carbonyl]amino[sulfonyl]methyl-
benzoate and 0.46 propylene glycol were mixed and
2.02 g technical toluene diisocyanate (80% 2,4-isomer
and 20% 2,6-isomer) containing 0.039 g dibutyltin
dilaurate was added. The cured product contained
15 2.9% active ingredient. The release rates were 10%
in 162 hours and 16% in 451 hours. Similar results
were obtained when 2.0 g of a solution of 50%
technical toluene-2,4-diisocyanate and PAPI® 901 was
used instead of technical toluene-2,4-diisocyanate
20 alone.

EXAMPLE 8

Krovar® I (9.0 g) water-dispersible granules
(E. I. du Pont de Nemours & Co.), containing 40%
bromacil and 40% diuron, was treated successively
25 with 0.2 g propylene glycol and 0.51 g PAPI® 901
containing 0.4% dibutyltin dilaurate. The release
rate of the bromacil in the granules in excess water
was 76% in 21 hours and 83% in 46 hours. The
granules maintained their integrity over one month in
30 excess water while continuing to release bromacil.
The uncoated control granules disintegrated and
released all of their bromacil in less than one hour.

CLAIMS

BA-8820

What is claimed is:

5

1. A process for preparing controlled release granules of pesticides for direct application consisting essentially of overcoating a granular carrier containing a pesticide and a polyhydroxylated compound, mixtures of polyhydroxylated compounds, or mixtures of water and at least one polyhydroxylated compound or water alone with a liquid polyisocyanate or mixture of polyisocyanates and, optionally, a polymerization catalyst, resulting in an interfacial polymerization reaction to a solid cross-linked polyurethane or polyurea barrier.

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2. The process of Claim 1 which takes place at elevated temperature.

3. The process of Claim 1 wherein the pesticide is a herbicide or insecticide.

4. The process of Claim 3 wherein the herbicide is selected from sulfonylureas, imidazolinones, uracils, dinitroanilines and the insecticide is a phosphorothioate.

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5. The process of Claim 1 wherein the granular carrier is selected from sand or aggregated clays.

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6. The process of Claim 5 wherein the granular carrier size is about 150 to 4,000 microns.

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7. The process of Claim 1 wherein said
polyhydroxylated compound is selected from ethylene
5 glycol or propylene glycol.

8. The process of Claim 1 wherein the
polyisocyanate is a methylene-linked
polyphenylisocyanate.
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9. The process of Claim 1 wherein the
polyisocyanate is a toluene diisocyanate.

10. The process of Claim 1 wherein the
15 polyisocyanate is a mixture of methylene-linked
polyphenylisocyanate and a toluene-2,4-diisocyanate.

11. The process of Claim 1 wherein the
polymerization catalyst is selected from organic
20 tertiary amines and alkyltin carboxylic esters.

12. A process for preparing controlled
release granules of pesticides for direct application
consisting essentially of adding a polyisocyanate or
25 polyisocyanate mixture and a polymerization catalyst
to granules containing a pesticide and water or
polyhydroxylated compounds or mixtures thereof at at
least about ambient temperature wherein the amount of
polyisocyanate and polymerization catalyst employed
30 are about 1 to 20% and 0 to 5% by weight,
respectively, resulting in an interfacial
polymerization reaction to a solid cross-linked
polyurethane or polyurea barrier whereby the amount
of said water or polyhydroxylated material is present
35 in an amount to insure that all of the polyisocyanate
has reacted.

13. The process of Claim 10 wherein the
5 reaction time is about 20 to 30 minutes.

14. The process of Claim 10 wherein the
pesticide is a herbicide.

10 15. The process of Claim 12 wherein the
herbicide is selected from sulfonylureas,
imidazolinones, uracils or dinitroanilines.

16. The process of Claim 10 wherein the
15 pesticide is an insecticide.

17. The process of Claim 10 wherein the
insecticide is a phosphorothioate.

20 18. The process of Claim 10 wherein the
granular carrier is selected from sand or aggregated
clays.

19. The process of Claim 14 wherein the
25 granular carrier size is about 150 to 4,000 microns.

20. The process of Claim 10 wherein said
polyhydroxylated compound is selected from ethylene
glycol or propylene glycol.

30 21. The process of Claim 10 wherein the
polyisocyanate is a methylene-linked polyphenyl-
isocyanate, or a toluene diisocyanate or mixtures
thereof.

22. The process of Claim 10 wherein the
polymerization catalyst is selected from organic
5 tertiary amines and alkyltin carboxylic esters.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/00015

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: A 01 N 25/26 //(A 01 N 25/26, 25:12)														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; text-align: left;">Classification System</th> <th style="border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">A 01 N</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	A 01 N								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border: 1px solid black;">Category *</th> <th style="width: 60%; border: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; border: 1px solid black;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">X</td> <td style="border: 1px solid black; vertical-align: top;">STN International, File CA, Chemical Abstracts, volume 112, no. 9, 26 February 1990, (Columbus, Ohio, US), abstract 72343t, & JP, A, 01056601, (KUMIAI CHEMICAL INDUSTRY CO., LTD.) 3 March 1989 --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-22</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">STN International, File CA, Chemical Abstracts, volume 100, no. 19, 7 May 1984, (Columbus, Ohio, US), abstract 152503n, & JP, A, 58205536 (NIPPON POLYURETHANE INDUSTRY CO., LTD.) 30 November 1983 --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-22</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">X</td> <td style="border: 1px solid black; vertical-align: top;">Patent Abstracts of Japan, Vol 9, No 74, C273, abstract of JP 59-206302, publ 1984-11-22 KUMIAI KAGAKU KOGYO K.K. --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-22</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	STN International, File CA, Chemical Abstracts, volume 112, no. 9, 26 February 1990, (Columbus, Ohio, US), abstract 72343t, & JP, A, 01056601, (KUMIAI CHEMICAL INDUSTRY CO., LTD.) 3 March 1989 --	1-22	A	STN International, File CA, Chemical Abstracts, volume 100, no. 19, 7 May 1984, (Columbus, Ohio, US), abstract 152503n, & JP, A, 58205536 (NIPPON POLYURETHANE INDUSTRY CO., LTD.) 30 November 1983 --	1-22	X	Patent Abstracts of Japan, Vol 9, No 74, C273, abstract of JP 59-206302, publ 1984-11-22 KUMIAI KAGAKU KOGYO K.K. --	1-22
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³												
X	STN International, File CA, Chemical Abstracts, volume 112, no. 9, 26 February 1990, (Columbus, Ohio, US), abstract 72343t, & JP, A, 01056601, (KUMIAI CHEMICAL INDUSTRY CO., LTD.) 3 March 1989 --	1-22												
A	STN International, File CA, Chemical Abstracts, volume 100, no. 19, 7 May 1984, (Columbus, Ohio, US), abstract 152503n, & JP, A, 58205536 (NIPPON POLYURETHANE INDUSTRY CO., LTD.) 30 November 1983 --	1-22												
X	Patent Abstracts of Japan, Vol 9, No 74, C273, abstract of JP 59-206302, publ 1984-11-22 KUMIAI KAGAKU KOGYO K.K. --	1-22												
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 16th April 1991 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 16 April 1991 </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer </td> </tr> </table>			Date of the Actual Completion of the International Search 16th April 1991	Date of Mailing of this International Search Report 16 April 1991	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer 								
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International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer 													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4223070 (ALICE U. HAHN ET AL.) 16 September 1980, see the claims --	1-22
A	GB, A, 2007095 (HOECHST AKTIENGESELLSCHAFT) 16 May 1979, see the claims -- -----	1-22

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/00015**

SA 43943

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 23/03/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4223070	16/09/80	AU-B- 522925	01/07/82
		AU-D- 4664279	08/11/79
		CA-A- 1118647	23/02/82
		EP-A-B- 0005302	14/11/79
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		DE-A-B-C 2743485	29/03/79
		FR-A-B- 2404461	27/04/79
		JP-A- 54057595	09/05/79
		NL-A- 7809798	30/03/79

For more details about this annex : see Official Journal of the European patent Office, No. 12/82